ADVANCES IN BROMINE-BASED MERCURY EMISSION CONTROL AT DIFFERENT FRENCH WASTE INCINERATION PLANTS

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VGB WORKSHOP MERCURY CONTROL,
MELIA HOTEL BERLIN, JUNE 8 – 9, 2017
Special thanks for cooperation with Vosteen Consulting and SARPI-VEOLIA to

Dr. Alfred Grissinger,
Luc Zonnenberg,
Bert Horemans

from

Merquel™ (CaBr₂)

ICL-IP Largest Producer of Bromine and Bromine Compounds Worldwide
AGENDA

• SARPI-VEOLIA’s Hazardous Waste Incineration (HWI) in Europe

• Development of the BEMO-Technology with CURRENTA in 2000 - 2009

• SARPI-Application of the BEMO-Technology at Sedibex since 2016 (3 lines with wet FGD)

• SARPI-Applications at diverse HWI plants with dry FGD since 2014

• Experiences with the precipitation agent PRAVO®

• Influence of Sulfur

• Outlook
A network of dedicated plants, unique in Europe

- 2,5 million tonnes treated
- 2,500 employees
- 10,000 industrial clients
- 550 M€ revenue
- Over 60 operational locations
- 9 countries

- 14 lines of high temperature incineration with energy recovery: 800,000 T/an
- 5 secure landfill sites for stabilised waste: 320,000 T/an
- 18 water/hydrocarbon treatment plants: 400,000 T/an
- 9 physical-chemical treatment plants: 220,000 T/an
- 27 transfer stations
- 15 facilities dedicated to recycling of: solvents, used motor oil units dedicated to the recycling, vegetable oil, hydrocarbons, metals
- 2 thermal desorption units for depollution of soil
10 SARPI-Hazardous Waste Incineration sites in Europe

Testings of the BEMO-Technology already performed at 5 sites (with 10 lines in total)
Preserving the environment by tackling the most difficult pollutants

Supporting our clients to limit the environmental impact of their wastes

The most toxical and persistent pollutants (POPs, micro-pollutants...)

- Mercury containing waste
- Contaminated sites and soils
- Pyrotechnic waste
- Low level radioactive waste
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... speaking about Hazardous Waste Incineration
Invention of the BEMO-Technology in 2000 by Prof. Vosteen

Bromides (HBr, NaBr\textsubscript{aq}, CaBr\textsubscript{2,aq})
Spiking Mercury

Continuously and Discontinuously

at top of after burning chamber
100 ... 20,000 µg/Nm³ dry

at bottom of after burning chamber
500,000 ... 80 Mio µg/Nm³ dry

„Hg-bombs“ -> „Hg-clouds“
Bromine Based Mercury Abatement

German Patent DE 10 233 173
(assigned to CURRENTA GmbH & Co. OHG)

European Patent EC 1 386 655
(assigned to CURRENTA GmbH & Co. OHG)

Patents granted also in
USA, Kanada, Australia, South Africa, Korea and Japan
Injection of 4 small Hg-bombs of 26 g only into the ABC, causing \textbf{without bromide-addition} – 4 huge Hg(0)-peaks upstream of the tail-end SCR.

\begin{align*}
\text{Source: Diploma thesis Andreas Pohontsch (2000)}
\end{align*}
Injection of Hg Bombs of Increasing Size (5 ... 340 g every 5 minutes, in total 3.4 kg) under co-combustion of bromine rich waste

Source: Diploma thesis Rico Kanefke (2001)
Bromine far more effective than chlorine

**Bromine > 25 times more effective for Hg\textsuperscript{met} oxidation than chlorine, in waste incineration as well as in coal combustion**

(BAYER patent applications pending worldwide)

Mass ratio Br/Hg and achieved Hg removal rate in test spiking the boiler raw gas with 9,600 µg Hg_{total}/dscm

Spiking the boiler raw gas with 9600 µg Hg/Nm³ dry)

Mass ratio Br/Hg = 100 ... 500 needed ("without high dust SCR")

Source: Diploma thesis Rico Kanefke (2001)
Final Installation in 2009 (Dr. Rico Kanefke)
Final Installation in 2009 (Dr. Rico Kanefke)
Final Installation in 2009 (Dr. Rico Kanefke)

Storage Tank for CaBr$_2$-Solution and Pump Housing at Currenta
Final Installation in 2009 (Dr. Rico Kanefke)

Injection Lance for CaBr₂-Solution at Afterburning Chamber

Number of injection lances at the ABC varies between 1 and 3 (depending on the mixing situation)
blue line: CaBr2 52% to kiln

brown line: Hg(0) at scrubber exit

dark-red line: Hgtot at stack

Time axis (day/month/year)
Explanation of the control principle:
Bromide injection only when needed
Yearly means in 1999 - 2001

Yearly means in 2005 - 2016
Successful industrial applications of the BEMO-Technology not only within CURRENTA, but at EGLV’s central WWTP Bottrop - since 2004, i.e. more than 12 years
First external testings at the WWTP Bottrop already in December 2003 and June 2004
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Sarpi aide les industriels à réduire leurs émissions

Alors que tous ses incinérateurs de déchets industriels dangereux sont en passe d’être équipés de solutions de captage de traces de mercure, Sarpi Industries souhaite valoriser auprès de tiers le savoir-faire qu’il a développé en interne.
Filiale du groupe Veolia, Sarp Industries (Sarpi) est un acteur important du traitement de déchets dangereux et, notamment, de l’incinération. À ce titre, la société opère 14 lignes de déchets dangereux en Europe, dont 3 lignes exploitées chez Sedibex, au Havre. La société s’est engagée dès 2012 dans la mesure en continu de ses émissions de mercure, avec l’objectif d’assurer, qu’à tout moment, les émissions de mercure sont inférieures au seuil réglementaire. Pour cela, la société est partie à la recherche de solutions de traitement et a notamment retenu l’option d’intégrer dans son portefeuille de solutions la technologie brevetée BEMO du professeur allemand B. Vosteen.

Les installations de Sedibex sont régulièrement au-dessous des seuils d’émissions de mercure.
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HWI plant 1 with dry APC at a glance

- Rotary kiln with an annual capacity of 60,000 tons per year

HW waste
- Solid
- Pasty
- Liquid
HWI plant 2 with semi-dry APC at a glance

- Rotary kiln with an annual capacity of 60,000 tons per year

Injury of activated carbon and lime

HW waste
- Solid
- Pasty
- Liquid

Post-combustion chamber
Boiler
Quench (Spray Cooler)
Bagfilter
Droplet separator
Dévésiculeur

Rotary kiln

Scrubber

Stack

Scrubber off-water is recycled to the spray cooler
HWI plant 3 with semi-dry APC at a glance
Method at HWI plant 1
Overview

- Mercury emission control tests

ICL CaBr₂ 52% w.

Hg-bombs / HgCl₂ 1% Hg w.

Lime LHOIST SP8
AC NORIT GL50®

Upstream APC
Hg(0) / Hg(2+) / HgT

Downstream APC
HgT
Continuous monitoring of the mercury species \( \text{Hg}(0), \text{Hg}^{2+} \) and \( \text{Hg}_{\text{tot}} \) under harsh conditions in the raw gas upstream of the bagfilter.
Mercury oxidation already upstream of dry APC improves sorptive Hg removal at normal (undonated) AC towards 100%. Lowering the filter temperature slightly is advantageous.

The AC GL50 flowrate is also important!
Almost 100% Hg oxidation achieved with mass ratio Br/Hg > 300
Bromide need e.g. only:
3 IBC à 1000 liter CaBr$_2$ (52 %) per year
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The precipitation agents of PAN Chemie Dr. Fülöp and Vosteen Consulting are Precipan, PRAVO®100, PRAVO®200

These are inorganic liquid agents containing polysulfides and thiosulfate. The highest content of active sulfur has PRAVO®200. For mercury precipitation at wet FGD, only low injection rates are needed (e.g. < 0.5 liter/hour PRAVO® at 60.000 Nm³/h flue gas). An important initial step in such applications is the formation of highly reactive polysulfanes as H-S-S-S-S-H (PRAVO addition to the acidic milieu as performed at MSWI in Darmstadt, 3 lines since 2008); but PRAVO does also work effectively, when added to a basic/neutral scrubber stage (as performed in sewage sludge combustion at WWTP Karlsruhe – Neureuth, 2 lines since 2007/8).

References for successful industrial long-time applications at wet FGD:
- Municipal Solid Waste Incineration (Darmstadt)
- Hazardous Waste Incineration (Leverkusen, Fos-Sur-Mer, Sedibex)
- Sewage Sludge Combustion (Bottrop, Karlsruhe-Neureuth)
- Thermal Treatment of Contaminated Soils (Moerdijk)
- Bituminous Coal Combustion (Block 2 in München Unterföhring)
Tests in 2007/8

HSE MSWC Darmstadt
3 units (220 t waste/year)
Testings in 2007 (over 2 months)

Spiking Hg, NaBr, PRAVO®100
3 + 1 SCEM (Mercem)

WFGD-tower with 3 stages (design: von Roll)
PRAVO container for continuous addition to slightly acidic middle wFGD-stage at pH = 2 – 4

PRAVO, diluted 1:3
Experiments on Mercury Deposition at MHKW Darmstadt

Scheme MHKW Darmstadt

Flue gas cleaning consists of spray dryer, E-Filter, wet scrubber and SCR Denox- and Dioxin reduction stage.

Mercury deposition at MHKW Darmstadt takes place in the wet scrubber with acidic quenching stage and packed bed and neutral ring-jet-stage.

The washer fluid is neutralized externally and evaporated in the spray dryer.
Testings in 2008 (Dipl.-Ing. Ulrich Mielke)

Dosing curve of PRAVO®100 as measured at MSWI line to suppress mercury reemissions.
Testing PRAVO®200 at SWM in 2014
Versuchstag 4: 12.04.2016 – PRAVO200 – 4 l/h
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SARPI regularly performs 30 d sampling-probes on PCDD/F at all its lines (obligatory in France)

Punctual probes on PBCDD/F were performed, as well, confirming the findings of Funcke and Vehlow in the late 1990s.

\[ \text{PXDD/F} \]
- An increase of the Br/Cl ratio in the fired waste (e.g. by co-combustion of electronic waste containing brominated flame retardants) correlates with an increase of PBCDD/F concentrations (mainly low brominated congeners). Funcke 1997, 2012.
- As observed in the flue gas of waste incinerators, the bromine containing congeners are formed at the expense of the purely chlorinated PCDD/F. The total concentration of all PXDD/F (X = halogen) is not influenced by varying Br/Cl ratios. Funcke 1997, 2012, Vehlow 2012.
- No tetr- to octabrominated congeners and also no tetro- to octabrominated polychlorinated cogeners will be detected when using a sampling period of 6 h according to DIN/ EN 1948.

\[ \Sigma (Br + Cl) \% \]
- As compared to trial C6
- These findings (resulting from numerous co-combustion trials) are expected to be valid for coal-fired power plants - with and without pre-combustion bromide addition for enhanced mercury capture - as well. Funcke 2012.

\[ \text{PXDD/F raw gas concentrations of a test incinerator in relation to the total halogen input (trial C6 = 100 \%) and to the molar Br portion (\% of total Cl + Br) in 5 reference trials R1 - R5 and 9 co-combustion trials C1 - C9. Funcke 1997} \]
VOSTEEN Consulting

Dioxin Tests March 2000
- 5 test conditions (3 runs each) were carried out

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<th>Test Run #</th>
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<th>2</th>
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<td>PAC (lb/hr)</td>
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<td>Sulfur (lb/hr)</td>
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<td>PCDD/F ng/gPCDD/F*</td>
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<td>2.0</td>
<td>3.6</td>
<td>0.2</td>
<td>0.3</td>
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</table>

*Sulfur/PAC addition tests showed lowest Dioxin concentrations

Tests in March 2000 at a FDI (15,000 Nm3/hr) of BAYER Polymers LLC. Vosteen 2001b

(19) United States
(20) Patent Application Publication
(21) Publication Classification
(22) Abstract

**ABSTRACT**
The invention relates to a process and apparatus for the low-temperature and low-emissions co-incineration of highly halogenated wastes, in particular liquid wastes, in waste incineration plants having at least one combustion chamber, a waste feed hopper, a multiburner/monoburner combustor containing a single-stage or multistage abrasive scrubber and an abrasive scrubber, at which either or a corresponding secondary or tertiary scrubber tank structure, or a tertiary scrubber tank structure, or a tertiary scrubber tank structure, or a tertiary scrubber tank structure. The amount of sulfur is controlled substantially in proportion to the current halogen-lowering agent from the waste in the boiler fuel gas.
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VEOLIA activities global
VOSTEEN Consulting

SARPI will perform tests of the BEMO-Technology at Veolia’s MSWI sites starting in October 2017.
Prof. Bernhard Vosteen and Ric Ulrich, PE, presenting the VOSTEEN-Technology („BEMO“) at the VEOLIA Hazardous Waste Incineration site in Port Arthur, near Houston, TX (USA) - already in 2006, i.e. more than 10 years ago.